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Aggregation Behavior of Mono-endcapped Hydrophobically Modified Poly(sodium acrylate)s in Aqueous Solution

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Titration microcalorimetry and steady-state fluorescence spectroscopy have been used to study the aggregation of mono-endcapped hydrophobically modified poly(sodium acrylate)s in aqueous solution. Polymers with molecular weights varying between 800 and 31,700 were synthesized by radical polymerization using an initiator and chain transfer agent. The resulting polymers form hydrophobic microdomains in aqueous solutions. The following conditions were applied: no salt and pH 5 and 9, respectively; 1 M sodium citrate and pH 9. At pH 5 the critical aggregation concentration (CAC, the concentration at which microdomains are formed) increases with increasing molecular weight of the polymers. The concentration range for aggregation is about 0.2-2.4 mM. At pH 9 the carboxylic acid groups are deprotonated and electrostatic repulsions are introduced; therefore the concentration for aggregation rises to about 80 mM. Interestingly, in case of polymers having $M_n > 1400$ the CAC decreases with increasing molecular weight due to a counterion-concentration gradient toward the hydrophobic microdomain. Near the microdomain the counterion binding is increased, reducing the electrostatic repulsions and allowing for lower aggregation concentrations. In the presence of 1 M sodium citrate this anomalous trend is suppressed to a large extent; since the overall counterion binding is increased and the CAC is lower. The concentration for aggregation is then in the same range as at pH 5 in the absence of salt. © 2000 Academic Press

Key Words: micelles; mono-endcapped hydrophobically modified poly(sodium acrylate); isothermal titration calorimetry; steady-state fluorescence.

INTRODUCTION

Water-soluble polymers find numerous applications in industry, since they can strongly modify the rheological properties of aqueous solutions. Handles for fine-tuning these properties include the molecular mass, charge, and chemical structure of the polymeric backbone. An important class of macromolecules are the hydrophobically modified polymers. In past years extensive research has been focused on random hydrophobically modified polymers (1-8). For instance in the case of poly(sodium

acrylate) it was found that when the alkyl chains are long enough ($>C_9$) intramolecular microdomains are already formed at low concentrations (1). At higher polymer concentrations also intermolecular association takes place. Such intramolecular microdomains cannot exist in the case of mono-endcapped hydrophobically modified polymers, since these polymers have only one hydrophobic tail per polymeric backbone. Some studies have been performed on nonionic oligomers with one alkyl chain attached specifically at the end of the oligomer (9-12), but the largest oligomer contained eight ethylene oxide units. Nonionic polymers of higher molecular weight were also studied, but these all contain two alkyl chains specifically attached at the ends of the polymer chains (13-18). Therefore these molecules can associate both inter- and intramolecularly.

Herein we report the first systematic study of the aggregation behavior of mono-endcapped hydrophobically modified polyelectrolytes as a function of molecular weight of the polymeric backbone. The concentration at which these mono-endcapped hydrophobically modified poly(sodium acrylate)s form aggregates was determined using steady-state fluorescence spectroscopy and isothermal titration microcalorimetry. It is shown that the critical aggregation concentration depends strongly on the degree of counterion binding, degree of protonation, and molecular weight of the polymeric backbone.

EXPERIMENTAL

Materials. Mono-endcapped hydrophobically modified poly(sodium acrylate)s were prepared by radical polymerization using an initiator and chain transfer agent. The procedure has been described previously (19). The initiator, ditridecanoyl peroxide, was prepared from tridecanoic acid chloride using sodium hydroxide and hydrogen peroxide (20). Tridecanoic acid chloride was obtained by reacting tridecanoic acid with excess thionyl chloride (21). Tridecanoic acid was obtained from Aldrich and was used without further purification. The chain transfer agent, *n*-dodecylthiol, was obtained from Aldrich and was distilled before use. The monomer, acrylic acid, was obtained from Across and distilled before use. Due to the structure and properties of the initiator and chain transfer agent there are three possibilities for the linker between the hydrophobic tail and hydrophilic headgroup; a sulfur atom, an acid group, or no linker. For the

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low-molecular-weight polymers relatively much chain transfer agent has been used. Therefore the sulfur linker predominates. For the high-molecular-weight polymers only small amounts of chain transfer agent have been used. Therefore, there is mainly no linker. We assume that the acid linker is present only in small amounts. Non-hydrophobically modified poly(acrylate) was obtained from National Starch; the polymer was used without further purification. The carboxylic groups were converted into their sodium salts by increasing the pH to 9 with sodium hydroxide. The viscosity-averaged molecular mass was 8000 (22). Using the weight-averaged molecular mass and viscosity-averaged mass ratio of a similar polymer and assuming a polydispersity of 2, the number-averaged molecular mass was estimated to be 5100.

Pyrene (99% pure) was obtained from Aldrich and was used as received. It was dissolved in water and filtered at least 1 day after dissolution. This solution was then diluted once. No excimers were present, since steady-state fluorescence showed no peak near 450 nm, characteristic of pyrene excimers (23).

Sodium citrate was obtained from Merck and used as received. Solutions were prepared using doubly distilled water.

¹H-NMR. ¹H-NMR spectroscopy (Varian 300 MHz) was used to determine the number-averaged molecular weight of the mono-endcapped hydrophobically modified poly(sodium acrylate)s using the endgroup method (24). Recently this method has been proven to be reliable (25). The results are shown in Table 1.

GPC. The polymers were characterized by aqueous gel permeation chromatography using an ultraviolet detector set at 215 nm. Fractionated poly(sodium acrylate) standards were used to construct a calibration graph. The molecular weight distribution can be described by Schulz-Flory theory (26). The results are shown in Table 1.

Potentiometric titration. The pH was measured using an Orion Model SA 720 digital pH-meter. Stirred solutions of hydrophobically modified poly(sodium acrylate)s with M_n 800 and M_n 6700 were titrated with a concentrated HCl solution (pH \approx 0.23) at room temperature.

Steady-state fluorescence spectroscopy. Steady-state fluorescence spectroscopic measurements were performed using

a SLM SPF-500C spectrofluorometer equipped with a thermostated cell holder and a magnetic stirring device. The instrument settings were as follows: excitation wavelength, 335 nm; slit width, 1 nm. The emission spectrum was recorded from 360 to 410 nm (slit width, 1 nm; step size, 0.20 nm; filter 2). Pyrene was used as a fluorescent probe at concentrations lower than 10^{-6} M.

Samples were prepared by dissolving the desired amount of polymer in aqueous solutions containing about 5×10^{-7} M pyrene. Solutions were allowed to equilibrate for at least 24 h. Then the emission spectrum was recorded and the intensities of the first (at about 370 nm) and third (at about 385 nm) peaks were determined. Control experiments were performed with solutions that had been equilibrated for 24, 48, and 72 h. All the experimentally determined I_1/I_3 ratios were the same within experimental error.

Measurements were performed under the following conditions: pH 4.90-5.10, no salt; pH 8.60-10, no salt; pH 8.60-10, 1 M sodium citrate. All experiments were done at 298 K.

Microcalorimetry (27). An Omega isothermal titration microcalorimeter (Microcal Inc., Northampton, MA) was used to measure the enthalpies of the polymer aggregation. The procedure was as follows. Thirty aliquots containing 10 μ l of a polymer solution were injected into a sample cell initially containing solution S_1 . The polymer interacts with S_1 , and the resulting enthalpic effect is measured by comparing the differences in energy that have to be added to the measuring cell and to the reference cell (containing pure water) to keep both cells at a constant temperature. Concentrations were corrected for the added volumes. Microcal Origin software was used to process the data. All experiments were done at 298 K, unless stated otherwise.

RESULTS AND DISCUSSION

Potentiometric Titrations

Potentiometric titrations of weak polyacids are very complicated and protonation of and counterion binding to the acid groups depend on many parameters (e.g., molecular weight of the polymer, concentration, salt concentration, tacticity) (28). The degree of dissociation (α) of the hydrophobically modified mono-endcapped poly(sodium acrylate)s was calculated by using the difference between the amount of protons added and the number of protons free in the solution. At pH 8.5 or higher the degree of dissociation is assumed to be 100%:

$$\alpha = 1 - \frac{[\text{COOH}]}{[\text{COOH}] + [\text{COO}^-]} = 1 - \frac{[\text{H}^+]_0 + [\text{H}^+]_{\text{total added}} - [\text{H}^+]_{\text{free}}}{[\text{acid groups}]} \quad [1]$$

Herein α is the degree of dissociation, $[\text{H}^+]_0$ is the proton concentration at the beginning of the experiment (before any HCl was added), $[\text{H}^+]_{\text{total added}}$ is the amount of protons added, and

TABLE 1

Molecular Weight, Polydispersity Index, and Number of Monomeric Units of the Single-Endcapped Hydrophobically Modified Poly(sodium acrylate)s under Study

M_n from NMR	M_n from GPC	M_w from GPC	M_w/M_n	Number of monomeric units (from NMR)
790				6.6
1,490	1900	2700	1.4	14
3,020	3100	4300	1.4	30
6,720				70
12,480				131
31,710				336

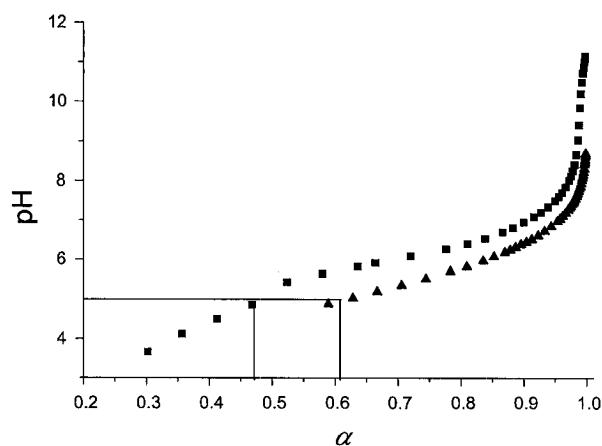


FIG. 1. Degree of dissociation (α) versus pH at 298 K. M_n 800, $[\text{polymer}]_0 = 15.5$ mM (■). M_n 6700, $[\text{polymer}]_0 = 19.9$ mM (▲). At pH 5 the degree of protonation of the polymeric backbone is 45 to 65%.

$[\text{H}^+]_{\text{free}}$ represents the concentration of free protons after every injection.

The main purpose of these potentiometric titration experiments was to determine the approximate degree of dissociation of the carboxylic acid groups at pH 5. From Fig. 1 it can be seen that the degree of dissociation at pH 5 is about 45 to 65%. Only a rough approximation for the degree of dissociation can be made.

Steady-State Fluorescence Spectroscopy

Since pyrene is a hydrophobic molecule, it partitions preferentially into an apolar environment (e.g., hydrophobic microdomains) (29, 30). The ratio of the intensity of the first peak and the third peak in the fluorescence spectrum is characteristic of the environment pyrene senses at its binding sites. In pure water this ratio is about 2, while this ratio is much lower in an apolar medium [e.g., hexane, 0.6; dodecane, 0.6; ethanol, 1.1; chloroform, 1.3 (31)]. In the hydrophobic microdomains formed by the polymers under study this ratio is circa 1.2 (32). The recorded value of I_1/I_3 is an average of that reported for pyrene in the microdomains and pyrene in the aqueous phase. However, since the equilibrium constant of pyrene in the aqueous phase and in micelles is of the order 10^6 M^{-1} (29), pyrene is expected to reside almost exclusively in the microdomains.

In the case of conventional surfactants (SDS, CTAB, etc.) one can plot the I_1/I_3 ratio against the concentration of surfactant to determine the critical micelle concentration (CMC) as the concentration where the I_1/I_3 ratio drops from 2.0 to 1.2. For surfactant aggregates this should occur over a rather narrow concentration range. However, this is not the case for polymeric surfactants (16–18). Here the I_1/I_3 ratio decreases over a larger concentration range; therefore two arbitrary borders were chosen. The ST (start of transition) indicates the concentration where the I_1/I_3 ratio drops below 1.7. The concentration where the I_1/I_3 ratio has dropped to 1.5 is called ET (end of transition).

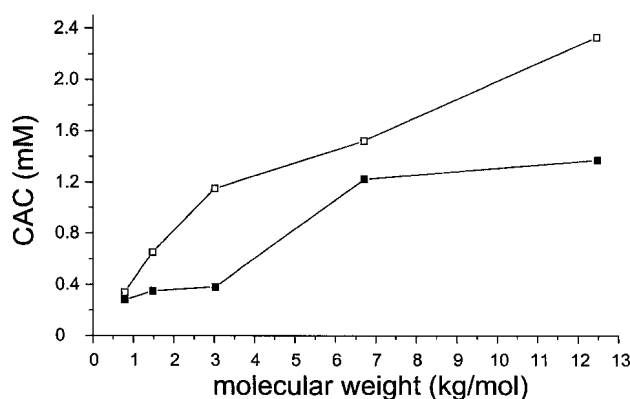


FIG. 2. Plot of CAC versus molecular weight determined by steady-state fluorescence, pH 5, 298 K, $[\text{sodium citrate}] = 0$ M: ST (■), ET (□). The lines are drawn to guide the eye.

Some spectroscopic probes are known to induce aggregation (30). Kevelam (24) compared the CMC of an anionic surfactant as determined using steady-state fluorescence spectroscopy, isothermal titration microcalorimetry, and conductivity and found that the CMC was the same within experimental error for the three techniques.

For all polymers under various conditions (salt/no salt, low pH/high pH) the I_1/I_3 ratios at the highest concentration employed were typically between 1.2 and 1.3, indicating that the hydrophobic domains formed are relatively apolar (micelle-like) (29). At pH 5 in the absence of sodium citrate the concentration range for aggregation is about 2 mM. From Fig. 2 it is clear that with increasing headgroup size (i.e., increasing molecular weight) the transition concentration increases.

The almost linear dependence of the transition concentration on headgroup size is similar to that found for conventional non-ionic (polymeric) surfactants (9, 10, 13, 16, 17, 33). From the literature and our potentiometric experiments it can be derived that electrostatic interactions between polymer backbones are reduced to a large extent at pH 5 due to protonation and counterion binding (34). (Fig. 3).

At pH 9 all the carboxylic acid groups are deprotonated. However, counterion binding is expected to be about 65% (30, 33, 35). We find that with increasing headgroup size the ST increases dramatically (Fig. 4) from 6.6 mM for the polymer with M_n 800 to 48 mM for the polymer with M_n 1500.

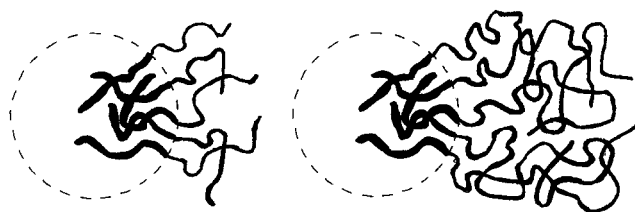


FIG. 3. Models for the polymer coil at pH 5 for a short polymer (left) and a long polymer (right). Like surfactants with a poly (ethylene oxide) headgroup a random coil is expected.

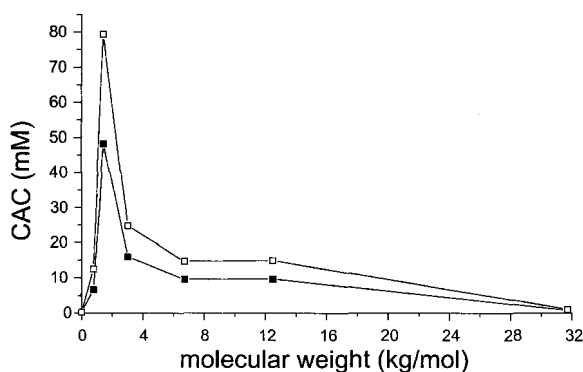


FIG. 4. Plot of transition concentration versus molecular weight as determined using steady-state fluorescence spectroscopy, pH 9, 298 K, [sodium citrate] = 0 M: ST (■), ET (□). The lines are drawn to guide the eye.

Due to the introduction of strong electrostatic repulsion there is a large increase in the concentration range for aggregation (up to about 80 mM). However, if the polymer molecular weight is increased beyond M_n 1500, this transition concentration decreases again with increasing molecular weight. This peculiar trend can be ascribed to a so-called “self-salting-out effect.” Near the hydrophobic domains the polymer chains are relatively close together, sensing a large electrostatic repulsion. This repulsion can be reduced only by an increase in counterion binding. Therefore fewer sodium ions are available for counterion binding to the end of the chains. However, the concentration of sodium counterions can be lower at the end of the polymers since the chains are further apart. The energetic strain associated with such a peculiar intrabackbone counterion distribution is less for higher-molecular-weight polymers, hence the CAC is lower. As illustrated in Fig. 5, the chains are expected to possess an extended coil formation.

At pH 9 and in the presence of 1 M sodium citrate, no distinct maximum in the ST or ET is observed (Fig. 6). The polymer of lowest molecular weight has a low ST (0.1 mM), but then the ST and ET remain more or less constant for polymers with

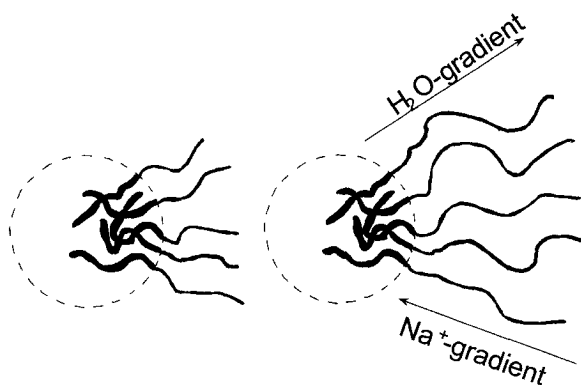


FIG. 5. Suggested models for the polymer coil at pH 9 for a short polymer (left) and a long polymer (right). Due to large electrostatic repulsion between the negatively charged acid groups the polymeric backbones are far from each other.

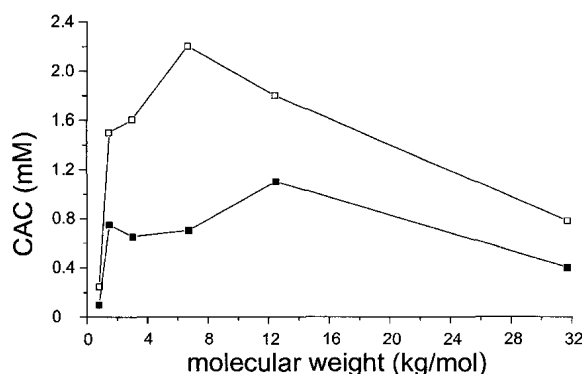


FIG. 6. Plot of CAC versus molecular weight determined using steady-state fluorescence spectroscopy, pH 9, 298 K, [sodium citrate] = 1 M: ST (■), ET (□). The lines are drawn to guide the eye.

M_n between 1500 and 12,500. The ST for the polymer with M_n 31,700 is somewhat lower.

By adding 1 M sodium citrate at pH 9 the transition concentration drops to about 1–2 mM, due to increased counterion binding and concomitant reduced electrostatic repulsion. However, since Fig. 6 does not exhibit a linear trend like that shown in Fig. 2 there still is some electrostatic repulsion left, and the “self-salting-out effect” is also reduced since no sharp maximum is observed at a characteristic molecular weight. This behavior can be rationalized in terms of a model that is a combination of the models suggested to operate for pH 5 and pH 9 in the absence of salt. The polymer chains will be sticking out into the solution due to electrostatic repulsion, but the coil will be less extended as that for the pH 9 solutions (Fig. 7).

Microcalorimetry

Isothermal titration calorimetry was employed as an additional probe-free technique to investigate the aggregation behavior of these hydrophobically modified polymers. The ST and ET obtained from the microcalorimetry experiments are labeled ST' and ET', respectively. In view of the fact that the details of the aggregation process at low concentration are not known we choose ST' and ET' rather arbitrarily (37). On injection of a small amount of a concentrated solution (S_1) into water (S_2) there is a characteristic heat effect. After every new injection of S_1 into

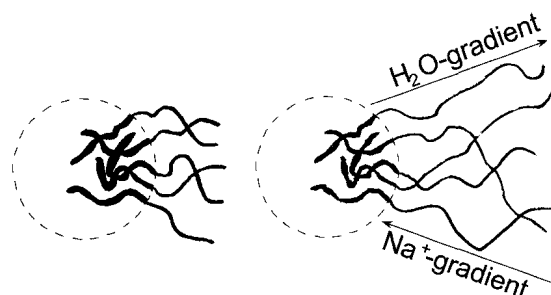


FIG. 7. Suggested models for the polymer coil at pH 9 in the presence of 1 M sodium citrate for a short polymer (left) and a large polymer (right). Electrostatic repulsion is largely reduced, but still present.

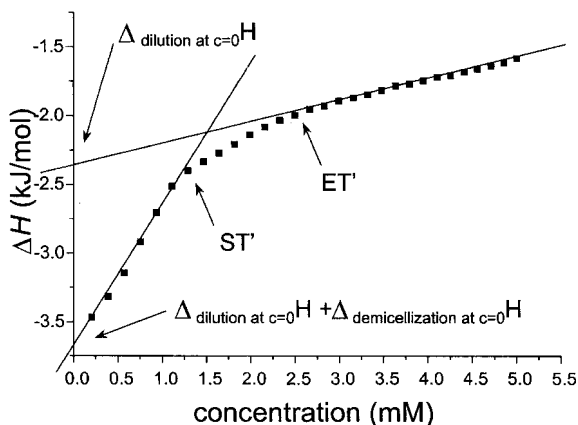


FIG. 8. Typical microcalorimetric titration experiment. M_n 3000, pH 9, 298 K, 1 M sodium citrate. Micellization is endothermic.

S_2 the heat effect is smaller since the concentration difference between S_1 and S_2 is smaller. This is the heat effect of dilution. In the case of S_1 being a concentrated surfactant solution there are two separate heat effects. Initially the micelles from the solution in the syringe break up, giving an additional heat effect. However, when the CAC is reached the micelles no longer break up completely and the heat effect of micellization diminishes, while the heat effect of dilution persists throughout the whole experiment. The data in Fig. 8 reveal that aggregation of hydrophobically modified poly(sodium acrylate)s is not highly cooperative (shown by the gradual disappearance of $\Delta_{\text{demic}}H$), so that aggregates grow between the ST' and ET' .

Microcalorimetry experiments with non-hydrophobically modified poly(sodium acrylate) have been performed to establish solely the enthalpic effects of polymer dilution. Straight lines for $\Delta_{\text{obs}}H$ as a function of polymer concentration are observed, providing additional evidence that the break in Fig. 8 obtained for hydrophobically modified polymers is due to (de)micellization (Fig. 9). The magnitude of the heat effects

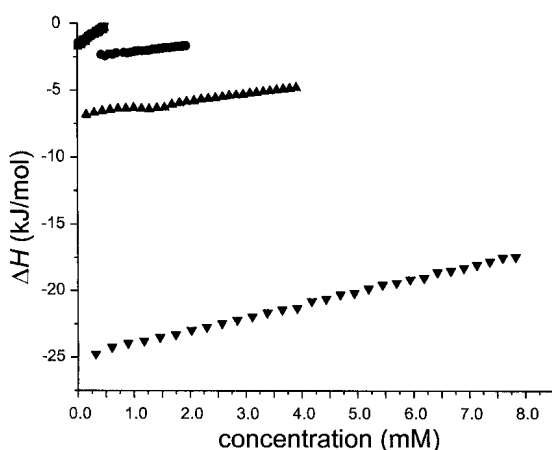


FIG. 9. Plot of ΔH versus concentration of poly(sodium acrylate) backbones having no hydrophobic endgroup (M_n 5100), 298 K: 1.25% w/w (■), 5% w/w (●), 10% w/w (▲), 20% w/w (▼).

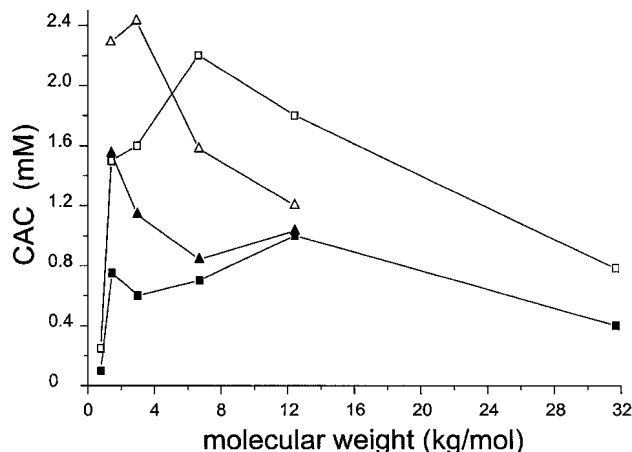


FIG. 10. CAC determined with both steady-state fluorescence and microcalorimetry. pH 9, 298 K, 1 M sodium citrate: $ST_{\text{fluorescence}}$ (■), $ET_{\text{fluorescence}}$ (□), $ST_{\text{microcalorimetry}}$ (▲), $ET_{\text{microcalorimetry}}$ (Δ). The lines are drawn to guide the eye.

shown in Fig. 9 is dependent on the concentration of the stock solution. This effect comes from the closer packing and hence the stronger interaction between solutes in a more concentrated solution (38).

In the case of the polymers with M_n 31,700 and 800 no well-defined ST' and ET' values were observed. For the short polymer the heat effect per injection was too small. For the longer polymer no break could be observed, as a result of relatively large heats of dilution compared with the heat effect of demicellization. For the other four polymers the ST' and ET' could be determined easily.

We conclude that the results of the steady-state fluorescence and microcalorimetry experiments are consistent with each other. The transition concentrations are of the same order of magnitude (Fig. 10) at both pH 5 and pH 9 (Table 2).

Figure 11 shows a typical dilution experiment at 50°C. Figure 12 shows the ST' and ET' values as a function of temperature. Throughout the temperature range, ST' and ET' remain about constant, except for the ET' at 30 and 35°C. This independence of the critical aggregation concentration on temperature has been observed for other surfactants as well (33, 39).

The heats of dilution and demicellization increase almost linearly with temperature, even becoming endothermic at 45°C (Fig. 13). At 25°C micellization is endothermic, showing that micellization is entropy driven, while at higher temperatures

TABLE 2
Comparison of Transition Concentrations as Determined Using Two Different Techniques

	pH 5, no salt, M_n 3000	pH 9, no salt, M_n 800
$ST_{\text{fluorescence}}$	0.4	6.6
$ET_{\text{fluorescence}}$	1.2	12.5
$ST_{\text{microcalorimetry}}$	0.5	5.0
$ET_{\text{microcalorimetry}}$	1.1	22.7

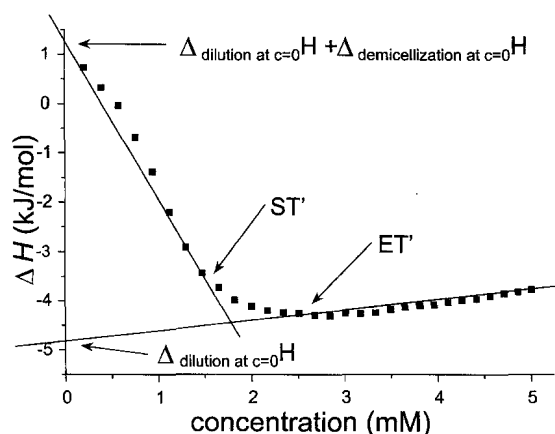


FIG. 11. Typical plot for the titration of hydrophobically modified poly(sodium acrylate)s into a 1 M sodium citrate solution at high temperatures (here 50°C), showing that $\Delta_{\text{mic}}H$ becomes exothermic with increasing temperature.

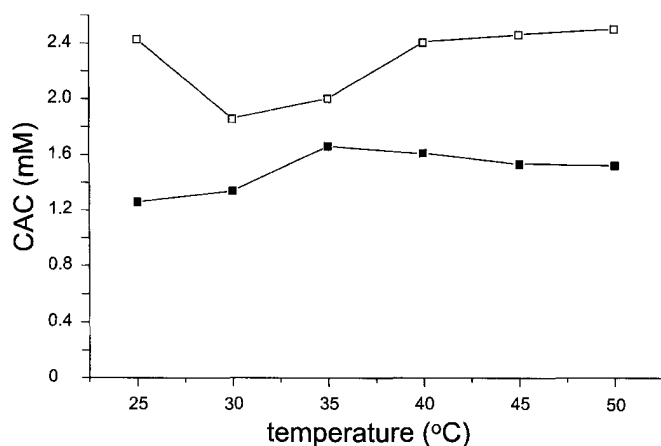


FIG. 12. Plot of CAC as a function of temperature: ST' (■), ET' (□). The lines are drawn to guide the eye.

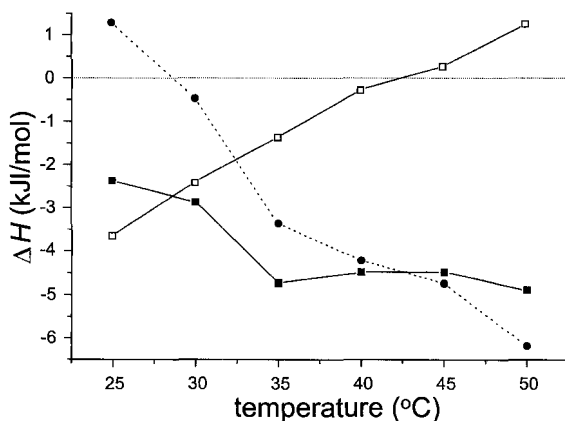


FIG. 13. Plots of ΔH versus temperature. M_n 3000, pH 9, 1 M sodium citrate: $\Delta H_{\text{dilution}}$ (■), $\Delta H_{\text{dilution}} + \Delta H_{\text{demicellization}}$ (□), $\Delta H_{\text{micellization}}$ (●).

micellization is exothermic, implying that micellization is enthalpy driven. The (almost linear) decrease in the enthalpy of micellization with temperature has been observed previously for ionic surfactants (33). From the dependence of the enthalpy of micellization on temperature it is clear that the heat capacities are negative as usually observed (38).

CONCLUSIONS

Hydrophobically mono-endcapped poly(sodium acrylate)s form hydrophobic microdomains in water. This is concluded on the basis of both steady-state fluorescence spectroscopic and isothermal titration microcalorimetric studies on poly(sodium acrylate)s with a linear C_{12} -alkyl chain attached specifically at the end of the polymer. However, there is no well-defined CMC, but rather a gradual transition from a micelle-free solution to a micellar solution. Steady-state fluorescence spectroscopy indicates that the microdomains are rather hydrophobic: the micropolarity at the pyrene binding sites is ethanol-like. At pH 5 in the absence of salt and at pH 9 in the presence of 1 M sodium citrate the CAC is in the range 0.2 to 2.4 mM. However, at pH 5 there is a linear increase in the transition concentration with headgroup size (i.e., molecular weight), due to an increase in steric and electrostatic repulsion between polymer main chains. At pH 9, in the absence of salt, the transition concentration is in the range 1 to 80 mM, with a sharp maximum in the transition concentration for the polymer of M_n 1500. This high transition concentration is caused by a large electrostatic repulsion between carboxylate groups, the fully ionized polymers have an extended coil conformation. For the larger polymers there is a so-called "self-salting-out effect," which consists of a concentration gradient of sodium counterions toward the hydrophobic domain, thereby increasing the sodium concentration near the hydrophobic core/hydrophilic corona interface and increasing the counterion binding and reducing the electrostatic repulsion at this interface. This effect is larger for the larger polymers because of the higher total sodium concentration and the less steep counterion concentration gradient. When polymer chains are in close proximity counterion binding is increased, whereas when polymer chains are far apart the counterion binding is reduced.

When salt is added the total counterion binding is increased. This lowers the electrostatic repulsion between the chains and reduces the transition concentration. The "self-salting-out effect" is also decreased, broadening the maximum found for the salt-free solutions and rendering the maximum less pronounced.

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